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(54) PRODUCING P-TYPE CONDUCTIVITY IN SELF-COMPENSATING SEMICONDUCTOR MATERIAL

(54) METHODE DE PRODUCTION DE MATERIAUX SEMICONDUCTEURS DE TYPE P A AUTO-COMPENSATION

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### ABSTRACT:

#### Abstract of the Disclosure

P-type self-compensated semiconductor materials and a process for producing them are described. The process includes imparting a region of P-type conductivity to the body of a self-compensated compound semiconductor material by the steps of preparing a crystal body of normally N-type self-compensated compound semiconductor material and bombarding said crystal body with charged particles such as beryllium ions.

### CLAIMS: [Show all claims](#)

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# PRODUCING P-TYPE CONDUCTIVITY IN SELF-COMPENSATING SEMICONDUCTOR MATERIAL

### Background of the Invention

4 Semiconductor materials of the compound type involving atoms from  
5 two different groups of the periodic table have been found to have many  
6 useful device properties. Many of these compound semiconductor materials  
7 have acquired the name intermetallics. Devices have been developed using  
8 compound type semiconductors where a particular property of the material  
9 is employed. However, in applying semiconductor device technology to  
10 compound semiconductor devices it is necessary to impart acceptor or  
11 p-type and donor or n-type conductivity to particular regions. There  
12 has heretofore been a number of the compound semiconductors that, while  
13 they had useful properties for devices, would exhibit only n-type con-  
14 ductivity. In these materials the conductivity effect of acceptor im-  
15 purities is overcome or compensated by the spontaneous generation of  
16 lattice defects which have donor type ionization levels. In the common  
17 case these lattice defects are vacancies. This phenomenon is known in  
18 the art as vacancy self-compensation.

### Description of the Invention

20 The invention involves introducing active, acceptor or p-type, con-  
21 ductivity sites into the crystal lattice by irradiation with electrons,  
22 protons or ions or by a combination of the introduction of p-type impuri-  
23 ties followed by electron, proton or ion bombardment. The resulting capability



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1 to produce p-type conductivity in compound semiconductor material enables  
2 one skilled in the art to employ the valuable properties of these materials  
3 which previously could only be obtained with n-type or insulating prop-  
4 erties to make a wide variety of structures, heretofore unattainable.  
5 For example, there are a number of compound semiconductor materials that  
6 exhibit n-type conductivity only, that have energy gap widths that would  
7 permit electrical to light energy conversion at frequency and colors  
8 not readily achieved in semiconductor devices. In accordance with the teaching  
9 of this invention the full range of semiconductor structures will now  
10 be possible with these materials.

DESCRIPTION OF THE DRAWING

12 FIG. 1 is an energy diagram of a compound semiconductor material  
13 that exhibits self-compensation.

14 FIG. 2 is a flow chart illustrating steps employed to impart  
15 p-type conductivity in accordance with the invention.

16 FIG. 2A is a more detailed flow chart illustrating steps employed  
17 to impart p-type conductivity with resistivity control in accordance with  
18 the invention.

19 FIG. 2B is a still more detailed flow chart illustrating the  
20 interrelationship between ion implantation and charged particle irradiation.  
21

22 FIG. 3 is a view of a two terminal semiconductor body having  
23 p-n junction therein.

#### DETAILED DESCRIPTION OF THE INVENTION

25 The class of materials to which this invention applies are those  
26 that could not be obtained with p-type conductivity heretofore because of  
27 the phenomenon of self-compensation. The phenomenon will occur when:

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1 Equation 1:  $E_c - E_v \geq \Delta H_f(v_B^x) + \Delta H_I(v_B^+)$

2 where  $E_c - E_v$  is the fundamental bandgap of the semiconductor material;

3  $\Delta H_f(v_B^x)$  is the enthalpy of formation of the neutral anion vacancy; and

4  $\Delta H_I(v_B^+)$  is the ionization enthalpy of the anion vacancy to its donor  
5 state.

6 Referring to FIG. 1 an energy diagram is provided to assist in  
7 illustrating the phenomenon of self-compensation in compound semi-  
8 conductors. The phenomenon occurs where the material generates enough  
9 lattice defects, commonly vacancies to compensate any concentration of impur-  
10 ties of the desired conductivity type. In practice the phenomenon has been  
11 observed to prevent p-type conductivity in large bandgap semiconductors  
12 where anion vacancies are more numerous than cation vacancies. The  
13 diagram shows the energy relationship of the maxima and minima of the  
14 valence and conduction bands, respectively, and the position of the  
15 fermi level. If the fermi level in this type of material were located  
16 near the valence band with a significant energy separation from a higher  
17 level which is the donor ionization level, then the total energy of  
18 the material could be lowered by generating an anion vacancy, ionizing  
19 same to its donor state, and allowing the resulting electron to drop to  
20 the fermi level. This process would cause the fermi level to rise away  
21 from the valence band, quenching p-type conductivity.

22 The energy separation between the donor energy level and the  
23 conduction band has been denoted in Equation 1 as  $\Delta H_I(v_B^+)$  and refers  
24 to the ionization reaction.

1      Equation 2:  $v_B^x \rightarrow v_B^+ + e_c^-$

2      where  $v_B^x$  and  $v_B^+$  are the neutral and ionized donor states, respectively,  
 3      of an anion vacancy  $v_B$  and  $e_c^-$  is an electron in the distribution of  
 4      states at the bottom of the conduction band.

5      Once the reaction of Equation 2 takes place the electron  $e_c^-$  may  
 6      fall to the fermi level releasing an energy  $E_c - E_f$ . Where  $E_c$  and  $E_f$  are  
 7      as defined in FIG. 1.

8      Assuming  $\Delta H_f(v_B^x)$  is the energy required to produce a new anion  
 9      vacancy, then if

10     Equation 3:  $E_c - E_f > \Delta H_f(v_B^x) + \Delta H_I(v_B^+)$

11     it will be apparent that it will be energetically favorable to create  
 12     more anion vacancies, ionize them and drop the resulting electron to  
 13     the fermi level.

14     As this occurs the fermi level will rise until

15     Equation 4:  $E_c - E_f \leq \Delta H_f(v_B^x) + \Delta H_I(v_B^+)$

16     at which condition self-compensation has taken place in the material  
 17     preventing p-type conductivity.

18     The phenomenon of self compensation has been observed thus  
 19     far in the art in at least the following compounds: gallium nitride (GaN);  
 20     aluminum nitride (AlN); zinc oxide (ZnO); zinc sulfide (ZnS); cadmium  
 21     sulfide (CdS) and cadmium selenide (CdS).

22     In accordance with the invention it is possible to impart  
 23     p-type conductivity to normally self-compensating compound semiconductors  
 24     that satisfy the conditions of Equation 1 by preparing a crystal of the  
 25     material in accordance with the desired dopants and then irradiating  
 26     the crystal with charged particles, for example, with electrons, protons  
 27     or ions. This may be contrasted with the normal ion implantation used to

1 convert conductivity type wherein the concentration of implanted impurities  
2 overwhelms the concentration of existing impurities. Such overwhelming is  
3 accompanied by a large amount of crystal damage which must be annealed out  
4 to reveal the effect of the doping level. The ion implantation technique  
5 produces wide junctions. In other words the invention rearranges the  
6 crystal atoms to produce conductivity whereas ion implantation relies on  
7 implanted atoms to control conductivity.

8 In the fabrication of semiconductor devices it is necessary to have  
9 resistivity control. This control is provided by the differences between  
10 FIGS. 2 and 2A.

11 Referring to FIGS. 2 and 2A flow charts are provided to illustrate  
12 the operations required in imparting p-type to a normally n-type compound  
13 semiconductor. The first operation is to prepare the normally n-type  
14 compound semiconductor crystal for charged particle irradiation. The  
15 preparation operation involves insuring that the crystal surface through  
16 which the irradiation is to take place is free of material that would  
17 inhibit or disturb evenness under the appropriate conditions for that  
18 operation. In instances where it is desirable to impart added flexibil-  
19 ity in resistivity control the preparation may include an added step of  
20 introduction of an acceptor impurity and may also be accompanied by  
21 inhibiting loss of donors through a coating.

22 Referring to FIG. 2 the flow chart sets forth a crystal prep-  
23 aration step, which in the broadest case consists of crystal surface  
24 condition control capable of permitting uniform, even, charged particle  
25 irradiation for example, by proton ( $H^+$ ) bombardment. The irradiation step  
26 consists of placing the crystal in a vacuum chamber under conditions such  
27 that a charged particle is supplied with sufficient electric field stress  
28 to insure penetration of the crystal to the desired depth and concen-  
29 tration. The necessary electric field stress is influenced by the mass

1 of the particle. In order to provide more dopant flexibility acceptor  
2 impurities can be first introduced prior to irradiation.

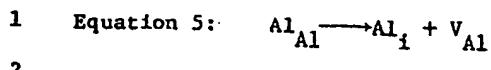
3 Referring to FIG. 2A the preparation step is expanded to include  
4 the use of a coating. The coating reduces loss of anion atoms during  
5 processing. When this coating is made of an acceptor and a charged  
6 particle irradiation is made therethrough, the acceptor concentrations can  
7 be enhanced in the step. Where appropriate the coating may also be  
8 used for contact metallurgy purposes in the final device.

9 Referring next to FIG. 2B the crystal is prepared for uniform  
10 introduction of dopants and charged particles through a surface thereof.  
11 Acceptors are then introduced into the crystal by the technique of ion  
12 implantation which may be followed by an annealing step. The crystal is  
13 then coated to reduce nitrogen vacancy loss in subsequent processing.  
14 The crystal is lastly irradiated with charged particles to convert to  
15 p-type.

16 In order to enable one skilled in the art to more easily comprehend  
17 the invention the following is an explanation as the state of the art  
18 has developed thus far, of the physics resulting from the steps and the  
19 structure, as applied to a particular material, aluminum nitride (AlN)  
20 using a particular charged particle, the proton ( $H^+$ ) for irradiation. It  
21 should be understood by one skilled in the art that the knowledge of  
22 physical mechanisms within compound semiconductor crystals is constantly  
23 evolving so that a particular physical mechanism should not be viewed as  
24 essential to the practice of the invention.

25 The light particle or proton bombardment is believed to create  
26 a situation where an atom of the crystal lattice is placed in an inter-  
27 stitial position leaving a vacancy in its substitutional site. This  
28 situation is known in the art as a Frenkel pair and is represented for the  
29 material AlN as

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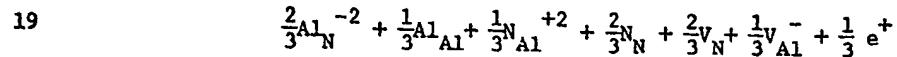
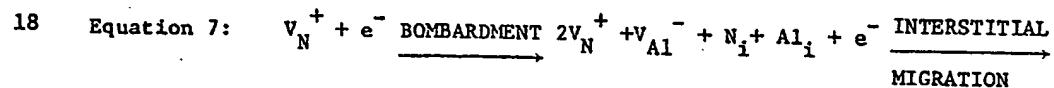


2 and



4 where  $\text{Al}_{\text{i}}$  and  $\text{N}_{\text{i}}$  refer to interstitial atoms,  $\text{V}_{\text{Al}}$  and  $\text{V}_{\text{N}}$  are  
5 neutral aluminum and nitrogen vacancies respectively and the sub-  
6 scripts Al and N denote the aluminum and nitrogen lattice sites  
7 respectively.

8 The interstitial atoms thus created migrate randomly through  
9 the crystal and would be expected to occupy the first vacant lattice site  
10 encountered. One can adjust the bombardment step so that the number of  
11 Al and N vacancies created will be essentially equal. When the number  
12 of bombarding protons ( $\text{H}^+$ ) is sufficient to create a number of Al  
13 vacancies and of N vacancies equal to the number of N vacancies initially  
14 present, the redistribution of interstitial atoms will override the  
15 vacancy self-compensation conditions in the crystal as set forth in  
16 equations 1 to 4 and a net p-type conductivity will result. The  
17 reaction is illustrated in the following relationship:



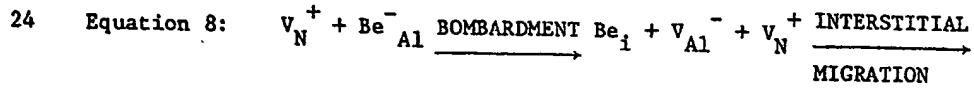
20 where  $\text{e}^-$  is an electron and  $\text{e}^+$  is a hole.  $\text{V}_{\text{N}}^+$  is the ionized  
21 nitrogen vacancy.  $\text{V}_{\text{Al}}^-$  is the ionized aluminum vacancy.  $\text{Al}_{\text{N}}^{-2}$  is an  
22 doubly ionized aluminum atom on a nitrogen site.  $\text{N}_{\text{Al}}^{-2}$  is a doubly  
23 ionized nitrogen atom on an aluminum site.

24 Where the concentration of N vacancies in the vacancy self-  
25 compensated compound semiconductor material before processing is less than  
26 that of other donor and deeply trapping impurities and defects already in  
27 the material or where lower resistivity values are desired, the vacancy

1 concentration can be increased as set forth in connection with FIG. 2A  
 2 where acceptor impurities in addition to those already present are added  
 3 to the material before bombardment. The acceptor impurities can be  
 4 incorporated during crystal growth, introduced by diffusion or added by  
 5 the ion implantation technique well known in the art. Considerable  
 6 flexibility is available with these techniques on depth and concentration.

7 The addition of acceptor impurities to the example material AlN  
 8 would increase the concentration of N vacancies. Prior to the conversion  
 9 step in Equation 7 the acceptor impurity level in the material would  
 10 be compensated but would be relatively shallow. The addition of  
 11 acceptor impurities will not only increase the concentration of nitrogen  
 12 vacancies but will enhance the p-type conductivity after the bombardment step.

13 An acceptor impurity for addition should be selected on the  
 14 basis of some of the following attributes. It should have a high solu-  
 15 bility in the material of the host crystal. It should act as a single  
 16 acceptor if located on an acceptor lattice site. It should act as a  
 17 triple acceptor if located on a donor lattice site. It should have a  
 18 sufficiently low mass that in reaction with the host crystal a low  
 19 bombardment threshold energy is required. Lastly, as an interstitial,  
 20 it should diffuse rapidly and not have the tendency to form interstitial  
 21 complexes. For the example material AlN, the acceptor impurity beryllium  
 22 is particularly attractive. The reaction in addition to Equation 7  
 23 for the ideal case would be as follows:



26 Referring next to FIG. 3 a p-n junction device fabricated in  
 27 accordance with the invention is illustrated. The device is made up of a

1 supporting substrate of an electrically and thermally conductive material  
2 such as copper to which an electrical lead 2 can be applied. The  
3 self-compensated compound semiconductor material member 3 is made up of an  
4 n-type conductivity region 4 and joined at a P-N junction 5 with a  
5 p-type conductivity region 6 to which is attached an electrical lead  
6 7. Where the member 3 is made of AlN, the n-type conductivity region  
7 4 is formed by the technique well known in the art of chemical vapor  
8 deposition wherein an AlN layer is deposited using a sintered AlN source.  
9 The region 4 is of low resistance n-type conductivity. A region 6 of  
10 beryllium (Be) doped AlN is sputtered on the region 4 until a depth of  
11 about 2000 angstroms is achieved.

12 The region 6 is then vacuum coated with a layer of beryllium  
13 (Be) 400 to 700 angstroms thick. The region 6 is then implanted with  
14 beryllium (Be) ions at a fluence of approximately  $10^{15}$  ions per square  
15 centimeter at a voltage of 140 kilovolts. This produces a p-type layer 6  
16 of approximately 2000 angstroms thick with a "hole" concentration of  $10^{19}$   
17 per CC, a mobility of about  $1000 \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$  and a resistivity of  
18 about  $10^{-3}$  ohms cm.

19 The beryllium, in addition to its being an acceptor dopant produces  
20 cation Frenkel pairs in a quantity great enough to convert the material.

21 It should be noted that the beryllium (Be) serves the role  
22 of a source of acceptors, the protective coating to prevent the out  
23 diffusion of nitrogen atoms, the charged particles in irradiation  
24 and the external electrical connection. Electrical connections 2  
25 and 7 are made to region 1 and the beryllium coating respectively.  
26 The resulting device when appropriately connected electrically performs  
27 such two terminal semiconductor device functions, such as asymmetric  
28 conductivity and electrical energy to light conversion.

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1        While a two terminal semiconductor p-n junction device has  
2        been shown it will be readily apparent to one skilled in the art that  
3        the teaching of imparting p-type conductivity of this invention is  
4        readily extendable to the range of semiconductor technology.